Supporting Information

Highly Efficient Non-Fullerene Polymer Solar Cells from Benzo[1,2-b:4,5-b']difuran-Based Conjugated Polymer with Improved Stabilities

Enfang He,# Zhi Zheng,# Yi Lu, Fengyun Guo, Shiyong Gao, Xinchang Pang, Genene Tessema Mola, Liancheng Zhao, Yong Zhang*

#Both authors contributed to this work equally.

1. Experimental Section

Materials: All chemicals and solvents were purchased from commercials and used directly without further purification except mention. The compounds and polymer were synthesized according to Scheme 1. 1-bromo-4-(2-butyloctyl) -3,5- difluorophene (1) and benzo[1,2-b:4,5-b']-difluran-4,8-dione, as well as TBz-Br were synthesized according to the procedure reported in the literatures.¹⁻³ The electron acceptor Y6 was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.



Scheme S1. The synthetic route of DiFPBDF-Tin.

Synthesis of 4,8-bis(4-(2-butyloctyl)-3,5-difluorophenyl)benzo[1,2-b:4,5-b']difuran (DiFPBDF)

To a solution of 1-bromo-4-(2-ethylhexyl)-3,5-difluorobenzene (2.0 g, 6.6 mmol) in dry THF under nitrogen atmosphere at -78 °C was added *n*-BuLi (2.4 M, 3.0 mL) dropwise. The mixture was stirred for 1 h at -78 °C and subsequently 4,8-dihydrobenzo[1,2-b:4,5-b']difuran-

4,8-dione (564 mg, 3.0 mmol) was added into the flask in one portion. The mixture was allowed to warm to room temperature gradually and stirred for 3 h. A mixture of $SnCl_2 \cdot 2H_2O$ (5.6g, 25 mmol) in 20% HCl (20 mL) was added into the mixture at 0°C and stirred for another 3 h at room temperature. Then the mixture was then poured slowly into ice water and extracted with diethyl ether, and the combined organic phases were dried over anhydrous MgSO₄ and concentrated to obtain the crude product. The product was then further purified by column chromatography on silica gel using petroleum ether as the eluent afford DiFPBDF as a white solid with a yield of 55%. ¹H NMR (500 MHz, CDCl₃, δ): 7.74 (d, 2H), 7.35 (d, 4H), 7.05 (d, 2H), 2.66 (d, 4H), 1.66-1.76 (m, 2H), 1.26-1.38 (br, 16H), 0.86-0.98 (br, 12H).

Synthesis of (4,8-bis(4-(2-butyloctyl)-3,5-difluorophenyl)benzo[1,2-b:4,5-b']difuran-2,6diyl)bis(trimethyl stannane) (DiFPBDF-Tin)

To a solution of 2a (0.97 g, 1.6 mmol) in dry THF at -78 °C was added n-BuLi (3 mL, 1.6 M) dropwise under a nitrogen atmosphere, the resulted mixture was stirred at -78 °C for 1 h, and then chlorotrimethylstannane (4.8 mL, 1.0 M) was added dropwise. The mixture was stirred overnight and allowed to warm to room temperature. Water (100 mL) was added, the mixture was extracted with diethyl ether three times, the organic layers were collected, dried over anhydrous Na₂SO₄, and evaporated to dryness under reduced pressure. The crude product was recrystallized from ethanol to afford DiFPBDF-Tin as a crystal (1.1 g, 71%).¹H NMR (500 MHz, CDCl₃, δ): 7.40 (d, 4H), 7.18 (s, 2H), 2.68 (d, 4H), 1.68-1.76 (m, 2H), 1.28-1.44 (br, 16H), 0.88-0.98 (br, 12H), 0.30-0.55 (br, 18H).

Synthesis of DiFPBDF-TBz (F13)

DiFPBDF-Tin (0.2 mmol) and TBz-Br (0.2 mmol) was mixed in 5 mL of toluene, and then the solution was purged with argon for 5 min. The catalyst, $Pd(PPh_3)_4$ (5 mg), was added in one portion, and the mixture was purged with argon for another 20 min. The reaction was then stirred at 110 °C for 6 h under argon protection. The polymer solution was cooled to room temperature and precipitated from 50 mL of methanol then collected by filtration and then subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The polymers were recovered as solid from the chloroform fraction by precipitation from methanol, and collected as metallic purple solid with a yield of 60% after dry in under vacuum.

F13: M_n= 7.96 kDa; M_w= 29.52 kDa; PDI = 3.7; ¹H-NMR (400 MHz, CDCl₃, δ, ppm): 7.90-7.56 (m, 4H), 7.38-7.15 (m, 2H), 7.10-6.78 (m, 2H), 4.5 (m, 4H), 3.6 (m, 2H), 2.81–2.32 (m, 5H), 1.68-1.31 (br, 42H), 0.92-0.76 (br, 18H).

2. Material characterizations

¹H NMR spectra were measured on a Bruker-AV 500MHz with d-chloroform as the solvent and trimethylsilane as the internal reference. UV-visible absorption spectra were measured via Beijing Purkinje General-TU-1901 spectrophotometer. Cyclic voltammetry was performed on a CH Instruments CHI660E electrochemical workstation with a three-electrode system in 0.1 M [Bu₄N]PF₆ acetonitrile solution at a scan rate of 40 mV/s. ITO with sample film was used as the working electrode. A Pt wire was used as the counter electrode and Ag/AgCl was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as the external standard and its redox potential is 0.45 V vs. Ag/AgCl. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potentials using the following equations: $E_{HOMO} = -e(\phi_{ox} + 4.35) (eV)$; $E_{LUMO}=^{E_{opt}}+E_{HOMO}$ (eV). Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode. Transmission electron microscopy (TEM) images of the polymer:*m*-ITIC blend films were recorded using a JEOL JEM-1400 transmission electron microscope operated at 120 keV.

3. Device fabrication and characterization

These PSCs devices were fabricated with the inverted structure of ITO/ZnO/active layer/MoO₃/Ag in a N₂-filled glovebox and characterized in the air without encapsulation. The ITO-coated glass substrates were cleaned with isopropyl alcohol, dishwashing liquid, deionized water, ethanol, acetone, and isopropanol for 30 min, respectively. The ZnO precursor

(concentration of solution: 0.45 M) was prepared by dissolving zinc acetate [Zn(CH3COO)₂·2H₂O] in 2-methoxyethanol containing ethanolamine as a stabilizer. The solution was stirred for 2-3 h at room temperature using a magnetic stirrer to obtain a homogeneous solution", which is according to the published work.^{4, 5} After being dried of ITO, the ZnO precursor (~20 nm) was spin-coated onto the cleaned ITO glass at 4000 rpm/min for 30s and annealed in the titanium plate under 250 °C for 30 mins. After ITO being dried, the ZnO precursor was spin-coated onto the cleaned ITO glass at 4000 rpm/min for 30s and annealed in the titanium plate under 250 °C for 30 mins. The active layer was spin-coated in a N₂-filled glovebox from a solution of F13:Y6 with 1: 1.5 weight ratio in chloroform with 0.5% 2chloronaphthalene (CN) as solvent additives. Subsequently, the active layers were undergone thermal annealing treatment at 130 °C for 2 min. Finally, 1 nm MoO₃ and 100 nm Ag were sequentially evaporated on the active layer in the vacuum chamber under a pressure of ca. 2.5 \times 10⁻⁴ Pa. The effective area of one cell is 4 mm². The current-voltage (J-V) characteristics of the devices were measured on a Keithley 2450 Source Measure Unit. The power conversion efficiency (PCE) was measured under an illumination of AM 1.5G (100 mW/cm²) using a SS-F5-3A (Enli Technology Co. Ltd.) solar simulator (AAA grade, 50 mm x 50 mm photobeam size). The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technololy Co. Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Hole-only device with the structure of ITO/PEDOT: PSS/F13:Y6/MoO3/Ag and the electrononly device with the structure of ITO/ZnO/F13:Y6/Ca/Al were fabricated. PEDOT:PSS (Heraeus Clevios P VP A 4083) was spin cast from aqueous solution at 3000 rpm for 30 s (40 nm), then dried at 150 °C for 15 min in air. 20 nm Ca and 100 nm Al were sequentially evaporated in the vacuum chamber under a pressure of ca. 2.5×10^{-4} Pa. ⁶ The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3}$$

Where *J* is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free soace, ε_r is the relative permittivity of the material, *d* is the thickness of the active layer, and *V* is the effective voltage.

4. Figures and Tables



Fig. S1. Cyclic voltammograms of (a) the F13 films on glassy carbon electrodes and (b) Ferrocene/ferrocenium in 0.1 mol L^{-1} Bu₄NPF₆ of acetonitrile solution at a scan rate of 40 mV/s



Fig. S2. The contact angles between organic blend films and the water droplet from front (a) and back (b)



Fig. S3. The ¹H NMR spectrum of the compound DiFPBDF-Tin.



Fig. S4. The light intensity dependence of Voc in F13:Y6 device.

D:A	E _g (A)[eV]	V _{oc} [V]	E _{loss} [eV]	Ref.
J81:ITIC	1.57	0.95	0.62	7
J81: <i>m</i> -ITIC	1.57	0.96	0.61	
PBDFT-Bz: <i>m</i> -ITIC	1.57	0.85	0.63	6
PBDFF-Bz: <i>m</i> -ITIC	1.57	0.94	0.72	
PBDFS-Bz:ITIC	1.57	0.82	0.75	8
PBDFS-fBz:ITIC	1.57	0.88	0.69	
PFBT-T:IT-M	1.57	0.89	0.68	9
PBDFTz-SBP:ITIC	1.57	0.89	0.68	10
L2:TTPT-T-4F	1.576	0.86	0.71	11
PBDFT-FBz: <i>m</i> -ITIC	1.57	0.81	0.76	12
PBDFF-FBz: <i>m</i> -ITIC	1.57	0.83	0.74	
F10: <i>m</i> -ITIC	1.57	0.91	0.66	13
F11: <i>m</i> -ITIC	1.57	0.92	0.65	
F13:Y6	1.34	0.815	0.525	This work

Table S1. The summary of E_g , V_{oc} and E_{loss} of polymer solar cells based on BDF polymers.

 Table S2. The photovoltaic perforamnce of F13:Y6 device at different aging time under nitrogen condition.

Time (hour)	Voc[V]	Jsc[mA/cm ²]	FF[%]	PCE[%]
0	0.80	22.61	70.28	12.71
48	0.80	22.87	72.00	13.17
192	0.80	22.89	71.96	13.18
744	0.815	23.27	70.37	13.34
840	0.812	23.15	70.96	13.34

936	0.81	22.95	70.90	13.18
1056	0.81	22.78	70.38	12.99
1224	0.807	22.72	70.00	12.84
1368	0.80	22.20	66.24	11.76

Table S3. The photovoltaic perforamnce of F13:Y6 device at different aging time under abmient air condition.

Time (hour)	Voc[V]	Jsc[mA/cm ²]	FF[%]	PCE[%]
0	0.78	23.20	65.38	11.83
24	0.80	22.41	69.31	12.43
48	0.80	22.24	67.57	12.02
72	0.80	22.00	67.75	11.93
120	0.79	22.12	68.62	11.99
216	0.79	22.09	68.30	11.92
312	0.77	21.89	68.37	11.52
360	0.78	21.96	65.54	11.23
744	0.78	21.87	65.26	11.13
1152	0.77	21.85	64.67	10.88

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